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(54) **Alumina coatings.**

(57) Anodized aluminum coatings employed in semiconductor processing equipment are treated to reduce their sensitivity to halogenated species. The pores of the aluminum oxide surface can be filled either by a metal, such as magnesium or aluminum, forming the corresponding metal oxide that is resistant to reaction with halogens, or by filling the pores with a getter for halogens, such as hydrogen ions. The hydrogen ions adsorbed on the surface of the

aluminum oxide react with halogens to form volatile hydrogen halides that can be pumped away in the exhaust system of the semiconductor processing chambers, thereby preventing or reducing reaction of the underlying aluminum oxide with the halogens.

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This invention relates to improved anodization processes and anodized aluminum coatings. More particularly, this invention relates to treated anodized aluminum coatings useful in harsh environments and processes for making the same.

BACKGROUND OF THE INVENTION

Aluminum metal is used in the semiconductor industry for parts and liners for various processing chambers including chemical vapor deposition and etch chambers. For example, substrate supports, susceptors, chamber walls and the like are made of aluminum metal. The aluminum becomes oxidized in air to form a thin native aluminum oxide coating thereon which is impervious to some of the chemical species generated in such chambers during standard processing. However, chemicals such as halides, e.g., bromides, chlorides and fluorides, are employed as etch and deposition gases, for example, and some of these processes are carried out in plasmas and/or at elevated temperatures. These chemicals will also etch or otherwise degrade aluminum and eventually the relatively thin native oxide coatings. Thus a thicker protective coating of aluminum oxide is desired.

Aluminum oxide coatings thicker than native oxide coatings can be made by anodizing the aluminum. Anodization can be carried out by making aluminum the anode and forming a suitable electrolyte in an electrolytic cell. Suitable electrolytes include inorganic acids such as nitric acid and sulfuric acid; or organic acids such as acetic acid or oxalic acid, for example. A DC voltage of 15-45 volts is applied until an aluminum oxide coating layer of the desired thickness over the aluminum metal is obtained, suitably about 0.0127 - 0.0508 mm (0.5 - 2 mils) thick.

Fig. 1A is a photomicrograph (110x) of the top surface of a grit blasted anodized aluminum surface that was anodized using oxalic acid. The aluminum oxide surface is quite uniform.

Fig. 1B is a photomicrograph (30,000x) of a cross section of an oxalic acid treated aluminum surface illustrating the somewhat porous, columnar structure of the aluminum oxide surface. Anodized aluminum is employed to protect aluminum parts from harsh etch environments. However, as shown in Fig. 1B, anodized aluminum is somewhat porous, and eventually the anodized coating is also attacked by harsh chemical species, particularly halogens, thereby exposing and etching away the underlying aluminum metal.

Fig. 2A is a photomicrograph (110x) of an oxalic acid anodized aluminum surface that has been exposed to a $\text{CF}_4/\text{N}_2\text{O}$ plasma at about 420°C for about 150 hours. It is apparent that the aluminum oxide has flaked away in many areas,

exposing the underlying aluminum metal surface.

Fig. 2B is a photomicrograph (110x) of an anodized aluminum part as in Fig. 1A which was scribed with a diamond scribe to damage the surface and thereby accelerate exposure of the surface to a halogen-containing plasma. After about 150 hours of exposure to $\text{CF}_4/\text{N}_2\text{O}$ plasma at 420°C, most of the aluminum oxide surface has deteriorated, and nodules evidencing halogen attack are present on the underlying aluminum surface. Thus these parts now must be replaced.

Various attempts have been made to treat anodized aluminum surfaces to prevent attack by halogen-containing species, but they are not suitable for use in semiconductor equipment used to process silicon wafers. For example, anodized aluminum has been "sealed" in boiling water, which probably adds oxygen in the form of OH^- groups to fill in the porous surface. However, moisture or residual OH^- groups tend to be released at high temperature and vacuum environments, which lead to undesirable reactions with halogens which can attack aluminum and silicon substrates, as well as other layers on the substrates.

Nickel has also been used to seal anodized aluminum pores, as by treating anodized aluminum surfaces with nickel fluoride or nickel acetate. However, nickel treatment is not suitable for semiconductor processing either because nickel can contaminate semiconductor substrates. US Patent 5,192,610 to Lorimer et al, assigned to the same assignee as the present invention, discloses a process of forming a protective coating of an aluminum oxide treated with a fluorine-containing gas.

In addition, various protective polymers have been coated onto anodized aluminum surfaces, but polymers cannot withstand plasma processing and/or the high temperatures employed in certain semiconductor processes such as chemical vapor deposition. The result is that the polymers degenerate and can flake off, causing particulates to form in the reaction chamber that will contaminate substrate surfaces, and reduce the yield of devices from these substrates.

Thus it would be highly desirable to be able to provide anodized aluminum coatings that are impervious to excited halogen species for comparatively longer periods of time, without attack of the underlying aluminum.

SUMMARY OF THE INVENTION

The invention is defined in claims 1, 2, 10, 12, 16 and 18, respectively.

We have found that anodized aluminum coatings can be treated to fill in the pores of the aluminum oxide, thereby making a less permeable surface that is more resistant to activated halogen

and other active species generated in a processing chamber. Such treatment increases the length of time that the treated anodized aluminum parts can be kept in service without replacement or re-anodization.

In a first embodiment of the present invention, anodized aluminum pores are filled in with a metal oxide and/or metal fluoride to reduce attack by active halogen species.

In another embodiment of the present invention, the pores of aluminum oxide are treated with a reducing agent. The reducing agent produces H^+ ions which are adsorbed on the surface of the aluminum oxide coating layer. These adsorbed H^+ ions getter materials such as halogen ions, forming gaseous or volatile HX products which can be readily removed from the processing chamber, thus eliminating or reducing attack of the anodized aluminum by active species.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1A is a photomicrograph of the top of an anodized aluminum surface.

Fig. 1B is a photomicrograph of a cross sectional view of an anodized aluminum surface.

Fig. 2A is a photomicrograph of an anodized aluminum surface that has been exposed to a halogen-containing plasma.

Fig. 2B is a photomicrograph of a damaged anodized aluminum surface that has been exposed to a halogen-containing plasma.

Fig. 3A is a photomicrograph of an anodized aluminum surface that has been exposed to a halogen-containing plasma.

Fig. 3B is a photomicrograph of an anodized aluminum surface that has been treated with a magnesium salt solution that has been exposed to a halogen-containing plasma.

Fig. 3C is a photomicrograph of an anodized magnesium-containing aluminum surface that has been exposed to a halogen-containing plasma.

Fig. 4 is a photomicrograph comparing a magnesium-treated and untreated areas of an anodized aluminum surface that has been exposed to a halogen-containing plasma.

DETAILED DESCRIPTION OF THE INVENTION

We have found that anodized aluminum surfaces can be treated to reduce their sensitivity to halogen species. The anodized aluminum surfaces can be treated either to reduce their porosity, e.g., to fill in the pores with another material that is relatively inactive to harsh semiconductor processing environments; or to provide an adsorbed getter on the surface of the pores to prevent harsh chemical attack of the anodized surface.

To further describe the first embodiment, anodized aluminum is treated to deposit a metal salt in the pores of the anodized aluminum. For example, the anodized aluminum part can be immersed in a soluble metal oxide salt solution such as magnesium acetate solution. The anodized aluminum part can be treated by immersing the part in a soluble magnesium salt solution, such as magnesium acetate, which wets the surface and fills in the pores of the aluminum oxide surface. When the magnesium acetate is heated, e.g., to about $550^\circ C$, the soluble magnesium salt decomposes to form an insoluble magnesium oxide, thereby filling the aluminum oxide pores with magnesium oxide. Magnesium oxide is not attacked by active halogenated species. For example, magnesium oxide can react with fluoride ions to form a nonvolatile magnesium fluoride (MgF_2).

The anodized aluminum part can also be treated to deposit aluminum oxide in the pores. For example, the anodized aluminum part can be treated with a colloidal suspension or an organoaluminum compound, such as aluminum secondary butoxide, in a solvent, e.g., butyl alcohol. After exposure of the treated part to elevated temperature, e.g., $200-500^\circ C$, aluminum oxide is formed in the pores of the anodized part.

Alternatively, aluminum oxide can be deposited by chemical vapor deposition (CVD). The anodized aluminum part is loaded into a chemical vapor deposition chamber and a suitable organoaluminum precursor gas fed to the chamber while maintaining the temperature of the part over about $200^\circ C$, preferably at above $350^\circ C$ or higher. Aluminum oxide is deposited into the pores of the anodized aluminum part, effectively sealing heat generated defects in the anodized aluminum surface.

To illustrate the protective effects of this mode of treatment, reference is made to Figs. 3A and 3B. Fig. 3A is a photomicrograph (110x) of a prior art oxalic acid anodized aluminum surface which was exposed to a CF_4/N_2O plasma for about 100 hours at $420^\circ C$. The original aluminum oxide coating has been largely replaced with halogen reaction by-products (aluminum fluoride) on the surface of the aluminum.

In accordance with the invention however, after formation of an anodized aluminum oxide surface using oxalic acid, the anodized surface was then treated with a soluble magnesium salt solution and magnesium oxide formed in the pores of the alumina. The surface was then exposed to the same plasma as above. In contrast to the surface shown in Fig. 3A, the surface of the magnesium-treated aluminum oxide remained uniformly coated with a protective aluminum oxide coating.

As a further comparison, Fig. 3C is a photomicrograph (110x) of a sulfuric acid anodized

aluminum surface wherein the aluminum was 6061 aluminum which contained a minor amount, about 1.2% by weight, of magnesium. However, the presence of only small amounts of magnesium was not sufficient to protect the anodized surface. Fig. 3C shows that an anodized 6061 aluminum surface that was anodized with sulfuric acid and exposed to the same plasma conditions as given above as for Fig. 3A was insufficient to provide protection for the aluminum and that the surface had badly deteriorated.

As an example of obtaining the improved anodized coatings of the invention in accordance with the first embodiment, the anodized aluminum part was treated with a soluble magnesium salt, such as magnesium acetate. The part, e.g., a susceptor, was then heated to a temperature sufficient to form magnesium oxide, e.g., about 400-550 °C, and preferably heated to a temperature of over about 402 °C. The resultant magnesium oxide bonded to the aluminum oxide under these conditions, which can form an excellent barrier layer for the underlying aluminum. Similar results are obtained by depositing aluminum oxide in the pores of the subject anodized coatings.

Magnesium oxide can optionally and preferably be treated with fluorine to form magnesium fluoride in the pores of the aluminum oxide. Magnesium fluoride expands during heating, thereby generating compressive stress. This compressive stress tends to mitigate the tensile stress which is inherent in aluminum oxide anodization because of the differences in the thermal coefficients of expansion and resulting mismatch between the magnesium oxide, the aluminum oxide and aluminum metal upon heating. These tensile stresses and thermal mismatch will cause cracks and other defects in anodized coatings, which also expose the underlying aluminum to attack by harsh processing chemicals.

Fig. 4 is a photomicrograph of an aluminum surface that was anodized in a first circular area, indicated as A, using oxalic acid to form an anodized aluminum surface. A second circular area, indicated as B, was first anodized using oxalic acid and then treated with magnesium acetate, heated to form magnesium oxide, which was then treated with fluorine. As shown in Fig. 4, the untreated region A is smoother and has less surface roughening. The anodized and magnesium treated aluminum surface was then exposed to a $\text{CF}_4/\text{N}_2\text{O}$ plasma for about 100 hours. It is also apparent that the untreated area has been attacked by the plasma more than the magnesium-treated area.

Preferably, the formation of magnesium fluoride from magnesium oxide is performed during normal chamber operations, as by treating the anodized aluminum having magnesium oxide-filled pores with fluorine at elevated temperatures be-

tween the processing of substrates. The magnesium fluoride film is advantageous because it is a thermodynamically stable compound with a low vapor pressure, which does not adversely affect the character of standard processing of semiconductor substrates such as silicon wafers.

Another advantage of the present method is that the magnesium oxide pore filler has a gettering effect on fluoride. The above processing with fluorine forms magnesium fluoride by reaction with the surface magnesium oxide molecules, leaving unreacted magnesium oxide below the magnesium fluoride surface. This unreacted magnesium oxide acts as a reservoir of getter material that will react with any fluoride (F^-) species that penetrate the surface magnesium fluoride, thereby further protecting the aluminum substrate from attack by halogens such as fluoride ions.

In order to carry out the second embodiment of the present invention, anodized aluminum surfaces are treated with a reducing gas, such as NH_3 . The reducing gas is a source of H^+ ions, which are adsorbed into the pores of the anodized aluminum. During semiconductor processing, the adsorbed H^+ ions act as getters for active halogens, forming HX for example. HX compounds are generally gaseous or at least volatile materials that can readily be removed from the processing chamber, as through the chamber exhaust system, before the halogen can attack the underlying aluminum.

To illustrate this process, after a standard plasma clean of an etch chamber, a plasma from NH_3 was formed in the chamber by passing ammonia into the chamber between processing cycles. Hydrogen ions formed in the plasma will adsorb onto the aluminum oxide surfaces. As another illustration, aluminum oxide parts in a chemical vapor deposition chamber can also be treated. In the case of silicon nitride for example, ammonia is already part of the reaction gases, which can continue to be passed into the chamber between deposition cycles.

The hydrogen ions can be supplied either separately from normal substrate processing, or, preferably, as part of a standard process. As one example, hydrogen was supplied from an ammonia plasma following a standard plasma clean step between substrate processing steps in a chemical vapor deposition chamber having an anodized aluminum susceptor. The H^+ ions were adsorbed into the cleaned pores, thus replacing or augmenting the prior art seasoning procedure used normally at this point. As another example, plasma enhanced chemical vapor deposition of silicon nitride coatings uses ammonia as one of the processing gases as a source of nitrogen. Thus by feeding in one of the processing gases, ammonia, prior to adding other deposition gases such as silane, the hydrogen ion

adsorption is carried out and the objectives of the present invention are accomplished without interrupting normal processing sequences.

Although the present invention has been described in terms of specific embodiments, various changes of reagents and processing conditions can be made without departing from the spirit of the invention, as will be known to one skilled in the art. Such changes are meant to be included herein and the invention is not to be limited except by the scope of the appended claims.

Claims

1. A method of treating anodized aluminum oxide layers to reduce their permeability to halogens during semiconductor processing comprising the step selected from the group consisting of filling the pores of the anodized layers with a metal salt that is unreactive with halogens and filling the pores of the anodized layers with reducing ions.
2. A method of treating anodized aluminum surfaces which comprises filling the pores of the aluminum oxide with a metal oxide that is unreactive with halogens.
3. A method according to claim 2, wherein said metal oxide is magnesium oxide.
4. A method according to claim 2, wherein said metal oxide is aluminum oxide.
5. A method according to claim 2, wherein said anodized aluminum surface is immersed in a soluble metal salt solution and heated to form the corresponding metal oxide.
6. A method according to claim 5, wherein said soluble metal salt solution is an aluminum organoxide in an organic solvent.
7. A method according to claim 3, wherein said magnesium oxide is treated with fluorine.
8. A method according to claim 4, wherein aluminum oxide is formed by chemical vapor deposition.
9. A method according to claim 8, wherein an anodized aluminum part is treated with an organoaluminum gas in a chemical vapor deposition chamber at an elevated temperature of about 200-500 °C.
10. A method of treating anodized aluminum surfaces to decrease their sensitivity to halogens which comprises treating the surface with a reducing agent whereby hydrogen ions are adsorbed in the pores of the aluminum oxide surface.
11. A method according to claim 10, wherein said reducing agent is ammonia.
12. A method of protecting aluminum parts for improved resistance to corrosion by halogen species which comprises
 - anodizing the aluminum with a strong acid electrolyte to form a protective layer of aluminum oxide;
 - exposing the aluminum oxide to a soluble metal salt solution that is non-reactive with halogens to fill in the pores of the aluminum oxide layer with said metal salt; and
 - heating the metal salt to form its metal oxide.
13. A method according to claim 12, wherein said metal oxide is magnesium oxide.
14. A method according to claim 12, wherein said metal oxide is aluminum oxide.
15. A method according to claim 13, wherein said magnesium oxide is treated with fluorine to form a surface magnesium fluoride layer in said aluminum oxide pores.
16. A method of treating anodized aluminum surfaces to prevent attack of anodized aluminum surfaces by halides comprising treating said anodized aluminum surfaces with magnesium fluoride.
17. A method according to claim 16, wherein said anodized aluminum can be heated to a temperature of from about 200-500 °C during said treating step.
18. A method of treating anodized aluminum surfaces to prevent attack of the anodized aluminum surfaces by chemical vapor deposition of aluminum oxide onto said anodized aluminum surface at a temperature of at least about 200 °C to seal thermally generated defects in the anodized aluminum surface.



FIG. 1A



FIG. 1B



FIG. 2A



FIG. 2B



FIG. 3A

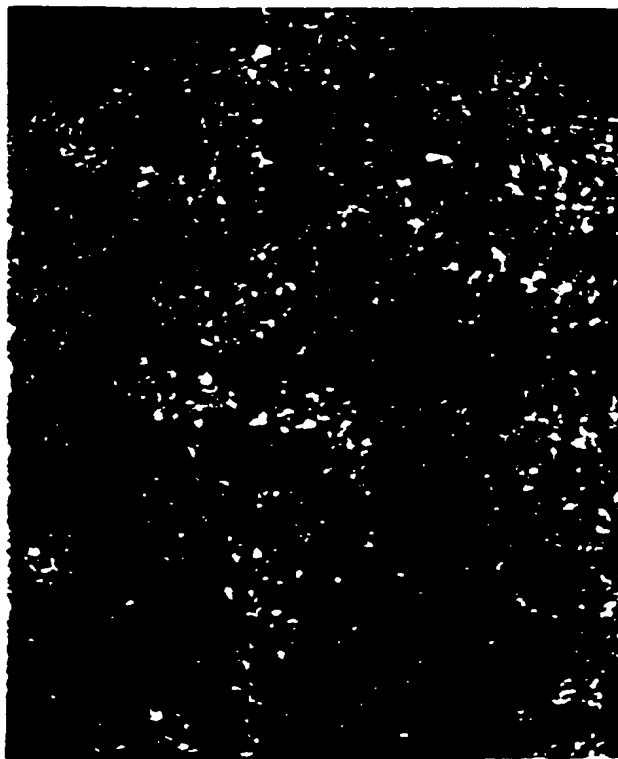


FIG. 3B



FIG. 3C

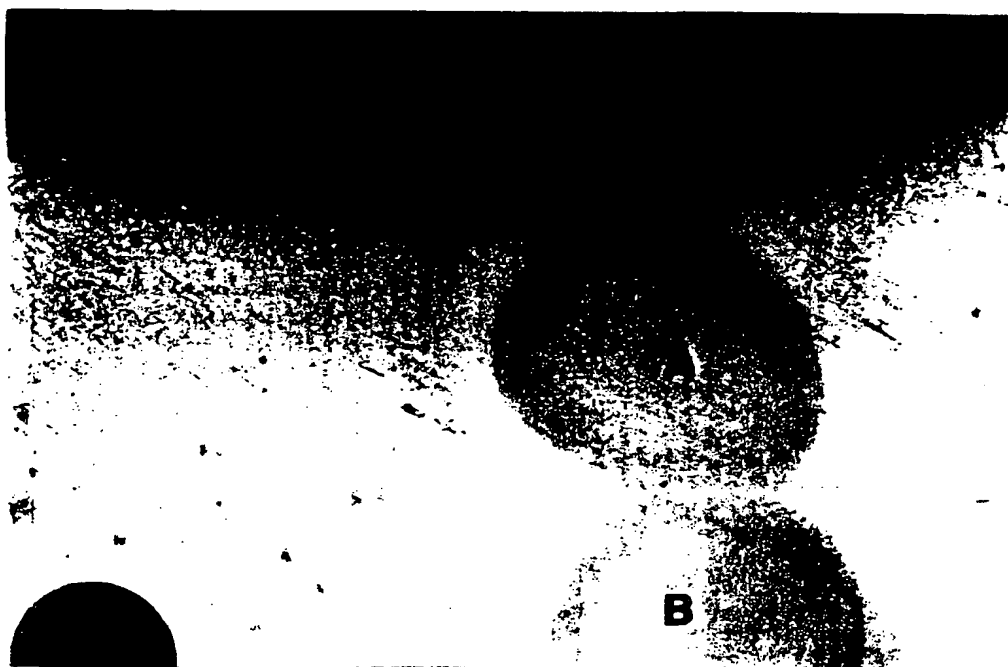


FIG. 4



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 6240

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION
X	PATENT ABSTRACTS OF JAPAN vol. 16, no. 118 (C-0922) 25 March 1982 & JP-A-03 287 797 (SUMITOMO ELECTRIC IND LTD) 18 December 1991 * abstract *	1-3, 5, 12, 13	C25D11/18
X	PATENT ABSTRACTS OF JAPAN vol. 12, no. 479 (C-552) (3326) 14 December 1988 & JP-A-63 192 895 (SUMITOMO ELECTRIC IND LTD) 10 August 1988 * abstract *	1-4, 8	
X	EP-A-0 410 003 (SUMITOMO ELECTRIC INDUSTRIES LTD) * page 5, line 22 - line 24; claims 4, 5 *	1, 2, 4-6	
			TECHNICAL FIELDS SEARCHED (Int. CL. 6)
			C25D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 January 1995	Examiner Nguyen The Nghiep, N
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure F : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	